Theory of alkali metal adsorption on close-packed metal surfaces

Catherine Stampfl and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany

Results of recent density functional theory calculations for alkali metal adsorbates on close-packed metal surfaces are discussed. Single adatoms on the (111) surface of Al and Cu are studied with the self-consistent surface Green-function method by which the pure adsorbate-substrate interaction may be analyzed. Higher coverage ordered adlayers of K on Al(111), Na on Al(111), and Na on Al(001) are treated using the *ab-initio* pseudopotential plane wave method which affords the prediction of coverage dependent stable and metastable adsorbate geometries and phase transitions of the adsorbate layers. Together, these studies give insight and understanding into current key issues in alkali metal adsorption, namely, the nature of the adsorbate-substrate bond at low coverage and the occurrence of hitherto unanticipated adsorbate geometries, and the associated electronic properties.

I. INTRODUCTION

Alkali metal adsorption systems have served as a theoretical paradigm for understanding the properties of adsorption on crystalline surfaces [1–10]. This is due to the simple electronic structure of the alkali metal atoms and also because it was understood that the adatom would not complicate the system of interest by intermixing with the substrate, but would stay on the surface and occupy a high-symmetry, highly coordinated position. Early experiments revealed that these "simple" adsorbates had a marked effect on the properties of the surface on which they were adsorbed [11]. For example, in the seminal work of Taylor and Langmuir [12] for the Cs/W system, it was shown that the work function of the clean surface is reduced by several electron volts on Cs adsorption and that at low coverage almost all the Cs adatoms are desorbed as positive ions. In the light of such results, the alkali metal bond to the substrate was viewed as a spectacular example of ionic bonding akin to that in alkali halides [13]. As a consequence of these distinct and general properties, alkali metal adsorption has come to play an important role in technological applications. For example, the desirable properties of the considerable enhancement of the electron emission of cathodes and the improved activity and selectivity of heterogeneous catalysts [14,15] are both achieved by the addition of alkali metal atoms to surfaces [16].

A simple picture of the interaction between alkali metal atoms and a metal surface, and of the resulting chemisorption bond was proposed by Langmuir [17]. He assumed that the alkali metal atom transfers completely its valence s electron to the substrate. In a more rigorous theoretical description of alkali metal adsorption Gurney [1], in 1935, proposed a quantum mechanical picture applicable at low coverages, where the discrete s level of the free alkali metal atom broadens (and shifts) becoming partially emptied as a result of the interaction with the substrate states as it approaches the surface (see Fig. 1). As follows from this picture the alkali metal atom is partially positively charged which induces a negative charge density in the substrate giving rise to an adsorbate induced dipole moment which naturally explains the reduction in the work function of clean surfaces. The building up of such adsorbate induced dipole moments also leads to the understanding that the dominant interaction between the adsorbates is repulsive and that the adatoms should form a structure with the largest possible interatomic distances compatible with the coverage. In this description it is expected that with increasing coverage the adsorbate-adsorbate distance gradually decreases, and the electrostatic repulsion between the adatoms increases. To weaken this repulsion, i.e., to lower the total energy, some fraction of the valence electrons flow back from the Fermi level of the metal to the adsorbate. Thus, a reduction of the adsorbate-induced dipole moment, i.e., depolarization takes place. This picture of Langmuir and Gurney has been held without question for many years.

The Langmuir-Gurney model was fully supported by systematic studies of Lang and Williams [4–6], who performed density functional theory calculations of isolated adatoms bonded to the surface of a simple metal ("jellium"), and by Lang's earlier work [2,3] on the alkali metal induced work function change. In these calculations the ions of the metal substrate were approximated by a semi-infinite uniform positive background which terminated abruptly along a plane, otherwise known as the "jellium" model. A jellium model was expected to represent well the electron density of a free-electron-like s-p bonded metal [18], and indeed these studies demonstrated that many ground-state properties of metal surfaces and metal-adatom systems can be described in a physically transparent manner. As an example, we show in Fig. 2 the change in work function with increasing coverage for parameters corresponding to Na on Al(111). The curve possesses a form similar to that often observed experimentally. This "usual" shape of $\Delta\Phi(\Theta)$ is explained as a consequence of the above-mentioned depolarization of the alkali metal induced surface dipole moment induced by continuous reduction of the adsorbate-adsorbate distance and corresponds to a rapidly decreasing work function at low coverage, reaching a minimum at about $\Theta = 0.15$, and subsequently rising towards the

value of the pure alkali metal.

The above description represents a sketch of the "traditional view" of alkali-metal adsorption, which, for example, is underlying the analysis of experimental results in various articles in the book of Bonzel, Bradshaw and Ertl [19]. However, since 1991 it has become clear through density functional theory studies [20,21], as well as through several experimental investigations, that the interactions and reactions of alkali metal atoms at metal surfaces are more complicated and exciting than hitherto expected. The calculations, which take the full atomic structure into account including relaxation of atoms from their ideal positions as well as surface reconstructions, show that the traditional view of alkali metal adsorption outlined above, is only part of the whole picture, and that we must now adopt an updated view. Phenomena such as the following may occur: 1) The alkali metal atoms may not necessarily assume highly coordinated sites on the surface [21–34]. 2) The alkali metal adatom may kick out surface substrate atoms and adsorb substitutionally [20,21,30–39]. Substitutional adsorption has been shown in three cases to occur as the result of an irreversible phase transition from an "on-surface" site by warming to room temperature, without change in the periodicity of the surface unit cell or of the coverage [32–38]. 3) The alkali metal atom may switch site on variation of coverage [29,31,40–43], and 4) island formation may occur [13,31,44–48]. 5) There may be a strong intermixing of the alkali metal atom with the substrate surface [49–52], as for example the formation of a four layer ordered surface alloy which had been identified for Na on Al (111) at a coverage $\Theta_{Na} = 0.5$ [51,52]. The coverage is defined in this paper such that for $\Theta = 1$, the number of adatoms is the same as the number of atoms in the clean unreconstructed surface layer. Alkali metal induced surface reconstructions are well known on the more open surfaces [53–55] as these clean surfaces are close to a structural instability [56]. But that significant reconstruction can occur on close-packed fcc (111) and (001) surfaces had not been expected previously.

The associated electronic properties of these hitherto unexpected surface atomic arrangements, perhaps not surprisingly, also exhibit behavior deviating from expectations based on early ideas. For example, experimental measurements of the change in work function as a function of alkali metal coverage can be quite different to the "usual" form of Fig. 2, for example, they may not exhibit a minimum at all, or may have a minimum at a significantly higher coverage. In the same manner, the density of states induced by alkali metal adsorbates may not always correspond to that expected from the model of Gurney.

Contrary to the idea mentioned above that the traditional picture be kept as representing *part* of a revised view, are recent theoretical studies which suggested a different picture of alkali metal adsorption be adopted [57,58]. In this picture there is practically no charge transfer from the alkali metal adatom to the substrate but rather a *polarization* of the adsorbate and the adsorbate-substrate bond is classified as covalent as opposed to the general and widespread understanding that it is of ionic nature at low coverages. This interpretation has seemingly been supported by experimental studies to the extent that it was concluded that the traditional picture be entirely discarded [59]. This is a controversial issue but we consider it a largely artificial conflict based on semantic differences. For a recent discussion we refer to Ref. [60,61], and a short summary of some of these arguments is given in Section III below.

The purpose of the present paper is to discuss results of recent *ab-initio* calculations for alkali metal adsorbates on close-packed metal surfaces. These density functional theory studies provide an accurate description of the microscopic electronic structure of the adatom as well as of the atomic geometry. In Section II we give a brief outline of the theoretical methods used. The results of Lang and Williams [5,6], Bormet *et al.* [61], and Yang *et al.* [62], for calculations of *single* adsorbates on jellium, on Al (111), and on Cu (111), respectively are discussed in Section III. These calculations afford an analysis of the nature of the adsorbate-substrate bond without it being obscured by the influence of other adsorbates. The results of these studies do not support a dismissal of the traditional view and the adoption of a covalent picture of alkali metal adsorption when adsorbed as isolated atoms. Rather, the results show that the traditional view is valid and useful but should only be applied in the limit of very low coverage and non-activated adsorption (see Section IV for the definition of activated and non-activated adsorption). The comparison of the results for different substrates enables one to establish the influence of the atomic structure and chemical nature of the substrate on the calculated quantities. In Section IV we discuss recent results obtained using the self-consistent pseudopotential plane wave method for higher coverages of alkali metal adsorbates on Al. From these calculations "unusual" adsorption sites and phase transitions have been predicted. The calculations also provide insight and understanding into the reasons why the unexpected adsorbate arrangements occur. In subsections IV A and IV B we discuss respectively, the coverage dependence of the adsorbate geometry, and the adsorbate-adsorbate and adsorbate-substrate bonding and the associated electronic properties. Section V contains the conclusion.

II. THEORETICAL METHODS

To provide some understanding of the two different calculation procedures, namely, the self-consistent surface Green-function (SSGF) method and the pseudopotential plane wave method, used to obtain the results discussed in the present paper, we give a short description of the theoretical basis. Both methods employ density functional theory (DFT) with the local density approx-

imation (LDA) for the exchange-correlation functional (DFT-LDA). We will first give an outline of this, then explain each of the calculation procedures separately. In the equations below Hartree atomic units are used.

A. Density functional theory

Density functional theory, as introduced by Hohenberg, Kohn, and Sham [63–65] has proved to be a conceptually and practically useful method for studying the electronic and atomic structure, as well as elastic and vibrational properties of many-electron poly-atomic systems. This theory represents a firm and exact theoretical foundation whereby all aspects of the electronic structure of a system in a ground state are completely determined by its electron density $n(\mathbf{r})$. The total energy of the ground state is given by

$$E^{\text{tot}}[n(\mathbf{r})] = T[n(\mathbf{r})] + \int V(\mathbf{r})n(\mathbf{r})\,d\mathbf{r}$$

$$+ \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + E_{xc}[n(\mathbf{r})] + E_{\text{ion}} \quad , \quad (1)$$

where $V(\mathbf{r})$ is the "external potential" due to the atomic nuclei (or the ion cores) and $T[n]$ is the kinetic energy functional for non-interacting electrons having the density $n(\mathbf{r})$. The functional $E_{xc}[n]$ contains all the quantum mechanical many-body effects and is called the exchange-correlation energy. Both $T[n]$ and $E_{xc}[n]$ are not known explicitly but at least the kinetic energy can be evaluated exactly when the density is written as a sum over orthonormal single-particle functions,

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \quad , \quad (2)$$

where N is the number of electrons in the system. This gives,

$$T[n(\mathbf{r})] = \sum_{i=1}^{N} \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \quad . \quad (3)$$

The variational property of the total energy then leads to the equation,

$$\{-\frac{\nabla^2}{2} + V_{\text{eff}}(\mathbf{r})\}\psi_i = \epsilon_i \psi_i \quad , \quad (4)$$

where

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (5)$$

which is to be solved self-consistently. The Hartree and exchange correlation potentials are,

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

and

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad .$$

The Coulomb energy associated with interactions among the M nuclei (or ions) at positions $\mathbf{R}_I$ is given by

$$E_{\text{ion}} = \frac{1}{2} \sum_{I,J,I\neq J}^{M,M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad . \quad (6)$$

The only unknown quantity is the exchange-correlation energy functional, $E_{xc}[n]$, and the quality of the solution of the full many-body problem is only limited by the quality of the approximation used for it. The exchange-correlation energy can be written as,

$$E_{xc}[n(\mathbf{r})] = \int \epsilon_{xc}[n(\mathbf{r})]\,n(\mathbf{r})\,d\mathbf{r} \quad . \quad (7)$$

A simple yet effective way to evaluate $E_{xc}[n]$ is to use the LDA [64] which means that the exchange-correlation energy density functional, $\epsilon_{xc}[n]$, is approximated by the corresponding expression for the homogeneous electron gas. That is,

$$\epsilon_{xc}[n] \equiv \epsilon_{xc}^{\text{LDA}}(n) \quad (8)$$

where $\epsilon_{xc}^{\text{LDA}}(n)$ is the exchange-correlation energy per particle of the many-body system which is known most accurately, namely, the uniform electron gas. Experience from numerous calculations show that for well bonded situations the LDA represents a good description of the quantum-mechanical many-body interactions in poly-atomic systems, and calculated electron densities, $n(\mathbf{r})$, atomic geometries, and total energy differences are in fact very reliable. In actual calculations, often some additional, more severe *numerical* approximations are applied. The latter can (and should) be carefully tested.

B. The self-consistent surface Green-function method

The self-consistent Green-function (SSGF) method is outlined briefly here and is presented in detail in Refs. [60,61,66]. It gives an accurate and efficient description for *isolated* adsorbates on *semi-infinite* substrates. Using this method the total and adsorbate induced density of states (DOS), charge densities and density differences can be obtained, as well as the total energy, total energy change, and forces on the adsorbate. In this approach the system is split into a *reference system* and a perturbative part with a perturbation potential, $\Delta V_{\text{eff}}[n]$, which has to be evaluated self-consistently. The reference system is taken to be the ideal, clean surface and the corresponding Green-function, G^0, is calculated employing the layer-Korringa-Kohn-Rostoker

(KKR) Green-function method [67]. The full Green-function of the adsorbate system is given by the Dyson equation,

$$G = G^0 + G^0 \, \Delta V_{\text{eff}} \, G \quad . \qquad (9)$$

Subtracting G^0 from both sides of equ. 9 gives,

$$\Delta G = G - G^0 = G^0 \, \Delta V_{\text{eff}} \, G \qquad (10)$$

$$= G^0 \, \Delta V (1 - G^0 \, \Delta V_{\text{eff}})^{-1} G^0 \quad . \qquad (11)$$

The perturbation potential, ΔV_{eff}, is written as,

$$\Delta V_{\text{eff}}[n(\mathbf{r})] = V_{\text{eff}}[n(\mathbf{r})] - V^0 \quad , \qquad (12)$$

where V^0 is the potential defining the reference system and the Green function G^0, and $n(\mathbf{r})$ is the density of the valence electrons. Thus, $V_{\text{eff}}[n(\mathbf{r})]$ is the functional of the effective potential as described by the Kohn-Sham equation (equs. 4 and 5). The perturbation potential, ΔV_{eff}, is strongly localized in real space. This localization allows equ. 11 to be solved efficiently in a rather small, localized basis set. In the work discussed below, s, p, and d gaussians and three different decay constants per angular momentum number are used which are centered on the adatom and on the three nearest-neighbor substrate atoms [61,62].

Once the change in the valence electron density is calculated self-consistently, the total energy, E^{tot}, as well as the forces, $F = \frac{dE^{\text{tot}}}{d\mathbf{R}}$, on the adsorbate as a function of its position $\mathbf{R}$ can be evaluated [61].

C. The *ab-initio* pseudopotential plane wave method

A very successful way to solve the Kohn-Sham single particle equation and to perform accurate calculations for a periodic system is achieved when ion cores are treated by *ab-initio* norm-conserving pseudopotentials and a plane waves basis set is employed. The great advantage of this approach is that the basis set is *unbiased*, i.e., the numerical accuracy can be tested systematically. Furthermore, it provides accurate forces on the atoms without complications typically encountered when other basis functions are used. The wave functions are written as,

$$\psi_j(\mathbf{k}, \mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| \leq G_{\max}} c_{j,\mathbf{G}+\mathbf{k}} \exp(i(\mathbf{G}+\mathbf{k}) \cdot \mathbf{r}) \quad , \quad (13)$$

where $\mathbf{G}$ are the reciprocal lattice vectors. Because the coefficients, $c_{j,\mathbf{G}+\mathbf{k}}$, for plane waves with high kinetic energy decrease and become negligible, the plane wave basis set can be truncated to include only plane waves that have kinetic energies less than some particular cutoff energy, $\frac{\hbar^2}{2m}|G_{\max}|^2 = E_{\text{cut}}$. Thus, the cutoff energy defines the quality of the basis set and it is one of the important numerical parameters of the calculations for which it must be carefully tested that they do not affect the results. In the pseudopotential plane wave method a crystal surface is modeled by a large supercell which contains a slab a certain number of atomic layers thick which is surrounded by vacuum. This supercell is repeated throughout space. The surface is then periodic in the plane of the surface on the scale of the supercell, but the periodicity perpendicular to the surface, imposed by the supercell, has no influence because for a sufficiently thick vacuum region the different slabs will not interact. However, care must be taken that the slab is thick enough so that its two surfaces are practically decoupled from each other. For a further description of the numerical details we refer to Refs. [21,68].

III. ISOLATED ADSORBATES

By studying *isolated* adatoms on surfaces the nature of the pure adsorbate-substrate bond can be analyzed. Self-consistent DFT-LDA calculations for isolated adatoms on a semi-infinite jellium surface have been performed by Lang and Williams [5,6]. Bormet *et al.* [61] carried out an analogous study for a representative set of isolated adsorbates on Al (111). In the latter work, instead of using a jellium model for the Al substrate, the atomic structure of the substrate is taken fully into account. Therefore, any significant differences in the results of the two studies is directly attributable to the treatment of the substrate. As a complementary study to the adsorbate on Al (111) systems, Yang *et al.* [62] investigated isolated adsorbates on Cu (111). From comparison with the results for Al (111), this work allows the influence of the Cu $3d$ electrons on the adsorbate bonding to be identified. In both of these latter calculations the self-consistent surface Green-function (SSGF) method was used. The set of adsorbates from the third row of the periodic table, were chosen in order to establish chemical trends. We concentrate here, in particular, on the case of alkali metal adsorption, but briefly describe the results for the other adsorbates, namely, Si and Cl in order to highlight the very different and characteristic behavior of the adsorbates which is found to be highly correlated with the electronegativity of the adsorbate with respect to the substrate.

A. Nature of the bond in the limit of very low coverage

For adsorption on Al (111) and Cu (111) the single adsorbates were placed in the fcc-hollow site, and in order to compare with the results of Lang and Williams [5,6], the surface was taken to be unrelaxed. This is, in fact, a good approximation because for non-activated adsorption the actual substrate relaxation is rather small.

4

The vertical height of the adsorbates was optimized by searching for the minimum of the total energy. From the study of Ref. [61] it was found that the equilibrium heights of the adsorbates above the surface are smaller for the Al (111) substrate than for the jellium substrate. With respect to the center of the top aluminum layer the heights are approximately 3, 20, and 20% smaller on Al (111) than on jellium for Na, Si, and Cl, respectively. For jellium the "center of the top layer" is defined to lie half a bulk inter layer spacing of Al (111) below the jellium edge. The larger values obtained in the jellium calculations are due to neglecting the atomic structure of the substrate which has the ability to bind the adsorbates more strongly. It is interesting that for Si on a jellium surface and using first-order perturbation theory for the crystal lattice, an equilibrium height is obtained which is identical to the full SSGF result [6,61]. On comparison of the results for adsorption on the Cu and Al substrates it is found that the jellium→aluminum trend continues: the effective radius of the studied adsorbates on Cu (111) is smaller than on Al (111) by approximately 11, 15, and 17%, respectively, for Na, Si, and Cl. Clearly, in this case it is more meaningful to compare effective radii than inter layer spacings due to the different lattice constants of Al and Cu. The smaller values reflect the existence of a stronger bonding of the adsorbates to the substrate for Cu (111) as compared to Al (111). This is identified as being due to the Cu d electrons [62].

Adsorbate induced density of states (DOS) and charge density difference plots are informative in discerning the nature of the adsorbate-substrate bond. The adsorbate induced DOS indicates whether the state of interest is occupied, unoccupied, or partially occupied, while charge density difference plots show whether there is a shift of charge density from the adsorbate towards the substrate, vise versa, or a sharing of charge between the adsorbate and the substrate.

The adsorbate induced DOS obtained from the SSGF calculations of Bormet et $al.$ [61] and those of Lang and Williams [6] for adsorbates on jellium, corresponding to a high electron density metallic substrate ($r_s = 2$ bohr), are shown in Figs. 3a and 3b, respectively. The adsorbates investigated in the work of Bormet et $al.$ [61] were Na, Si, and Cl and in that of Lang and Williams [6] they were Li, Si, and Cl. The results of both of these calculations agree qualitatively and may be interpreted as follows: For both Na and Li the adsorbate resonance lies well above the Fermi level and is thus largely unoccupied. This indicates that the valence electron of the alkali metal atom (or part thereof) has been transferred to the substrate and the adatom is partially positively charged. In an opposite manner, on adsorption of chlorine, the resonance in the curve corresponding to the Cl $3p$ resonance lies well below the Fermi level. Thus, this resonance is fully occupied which implies that a transfer of electronic charge density from the substrate to the Cl adatom has taken place; the adsorbed Cl atom is partially negatively charged. For the adsorption of an isolated Si atom it can be seen from the jellium calculations that the Si $3p$ resonance lies just at the Fermi level, which implies that it is about half occupied. Lang and Williams [6] have shown that the states of the energetically lower half of the p-resonance are bonding between the adatom and the substrate and that the energetically higher states are anti-bonding. Because the Fermi level cuts the p-resonance approximately at its maximum, the bonding nature of Si is covalent. The results for Si on Al (111) show also that the bond is covalent. In this case, however, more structure occurs in the DOS than in the jellium calculations. This arises because the atomic structure of the substrate leads to band structure effects (clearly reflected by the structure of the bulk DOS at E_F in Fig. 3a), and these induce a splitting of the bonding and anti-bonding states, and the adatom density of states exhibits a minimum at the Fermi level [61]. Similarly to the jellium substrate, the Fermi level cuts the Si $3p$ induced DOS roughly in the middle.

The behavior identified in the adsorbate induced DOS triggers the distribution of the valence electrons. In Fig. 4 we show the valence electron density for the chemisorption of Na, Si, and Cl on Al (111). The charge transfer from the Na atom to the substrate, as reflected by the adsorbate induced DOS, is clearly visible in Fig. 4 where it can be seen that there is an increase of the electron density between the Na adatoms and the topmost layer of the Al substrate, and that on the vacuum side of the Na atom the electron density has almost disappeared. For Si, as expected from the adsorbate induced DOS, a directional covalent bond is present between the Si adatom and the nearest-neighbor substrate atom. Furthermore, it can be seen that the maximum of the charge density of the chemisorption bond is closer to the more electronegative Si atom. In the case of Cl on Al the charge density distribution around the adsorbate is almost spherical.

In Fig. 5 we consider density difference plots. These plots display the electron density of the adsorbate system minus the density of the clean substrate and minus the electron density of the free adatom. The results for the Al and Cu substrates show a number of similar features, and some interesting differences. Firstly, it can be noted that in each case the perturbation to the system caused by the adsorbates does not reach very far into the metal substrate. The interior is essentially identical to that of the clean surface for layers deeper than the second. We emphasize that this localization holds for the electron density $perturbation$ but not for individual wave functions. For Na adsorption, perhaps the most noticeable feature is the charge cloud between the adsorbate and the substrate which reaffirms that charge is displaced from the vacuum side of the adsorbate towards the substrate side. These results are consistent with a partially positively charged adatom which sits on a negatively charged site. This constitutes a surface dipole which locally decreases the work function. The opposite situation is found for Cl, which is negatively charged and sits on an adsorption site that is positively charged. In

this case charge has moved from the substrate towards the Cl atoms and the local work function therefore will be increased relative to the value of the clean surface. For both substrates Si appears covalently bound with a slight electron transfer towards the adatom. Comparing in more detail the results for Al and Cu, we see that there is more charge between the Na adatom and the top layer of the Cu substrate. Also, there is a greater depletion of charge at the vacuum side. These effects are consistent with the fact that the electronegativity difference between Na and Cu $(0.93 - 1.90 = -0.97)$ is larger than that between Na and Al $(0.93 - 1.61 = -0.68)$. The Si atom, which clearly forms a covalent bond with both substrates, is slightly more electronegative than Al (by 0.27). In this respect, it can be seen that more charge resides on the Si atom when on Al than when on Cu for which the electronegativity difference is zero. The result for Cl on Cu displays some features similar Si on Cu, namely, the pile up of charge density between the Cl adatom and the nearest Cu atom. This structure is practically absent for Cl on Al. In all cases for the adsorbates studied, the adsorption on Cu exhibits some structure in the valence electron density change near the nucleus of the Cu atom closest to the adsorbate. This reflects the participation of the Cu d electrons in the bonding.

To summarize, Green-function calculations for single adatoms on jellium, Al (111), and Cu (111) substrates show qualitatively the same trend for the different adsorbates and this is well described by the adatom electronegativities compared to the electronegativity of the substrate atoms. For single alkali metal atoms on these surfaces, all the calculations support the charge transfer picture emphasized in the model of Gurney as providing a useful and appropriate description of the situation for alkali metal adsorption at very low coverage. Admittedly (see also Refs. [60,61]) the picture is useful and appropriate, but it is not unique. A (partially) charged entity in front of a metal surface will necessarily induce a screening charge density at the metal surface – the quantum mechanical realization of the image charge. This screening charge density is located between the adatom and the substrate surface. Therefore, from a purely mathematical point of view, the adatom induced electron density can be described in three different ways: i) in terms of orbitals of the adatom, ii) in terms of orbitals of the substrate, and iii) by taking both orbital sets into account. This ambiguity is due to the fact that the sum of the two Hilbert spaces of the adatom and of the substrate is over-complete. Whereas a mathematical analysis of the adsorbate induced electron density leaves this freedom, the chemical interpretation of the DOS, as well as its effect on the charge density, as discussed above, clearly support the qualitative picture of Gurney. We note, however, that this picture applies only to low coverages and an unreconstructed substrate. Otherwise, as will be seen in Section IV, some significant modifications take place.

IV. ALKALI METAL ADLAYERS ON AL

One of the interesting characteristics of alkali metal adsorption is the drastic change of several physical quantities as a function of coverage. The most obvious of these properties are perhaps the surface atomic geometry and the work function. With respect to the former, different commensurate phases are formed by alkali metal adsorbates on metal surfaces. Some of these structures can be understood as being due to a repulsive lateral adsorbate-adsorbate interaction, causing the adatoms to sequentially arrange into commensurate phases of ever growing compactness [13]. In addition, as mentioned in the introduction, behavior quite different to these arrangements has been reported, as well as a new class of unexpected geometries becoming evident, namely, those of *substitutional* and *surface alloy* structures.

To learn about the strong coverage dependence of the surface atomic arrangements and related properties, calculations for higher coverages of alkali metal adsorbates on metal surfaces have been performed for K on Al (111) [21,31,70], Na on Al (111) [21,31,51,70], and Na on Al (001) [36,37]. The calculations show that on increasing the coverage from very low coverage, where the alkali metal adatoms are uniformly spread over the surface, to higher coverages, the adsorbate-adsorbate interactions weaken the adsorbate-substrate bond because additional bonds are built up within the adlayer. We note that this is a general feature of bonding in poly-atomic systems: When the valence electrons are shared among many bonds, each single bond becomes weaker, and an increase of the bond length results. In the case of alkali metal adlayers this implies that a formation of lateral bonds in the adlayer will weaken the adsorbate-substrate bonds and increase the adsorbate-substrate bond length. This interplay/competition between adsorbate-adsorbate and adsorbate-substrate bond formation can give rise to interesting adsorbate arrangements and structural phase transitions. The results for the three systems are compared which affords changes due to different alkali metal atoms on the same surface to be identified as well as changes due to different substrate surfaces for the same adsorbate.

It is necessary to distinguish "non-activated" and "activated" adsorption. The former corresponds to adsorption on an only relaxed surface (small rearrangements of substrate atoms) where no energy barriers need to be overcome to reach the adsorption geometry. The latter refers to adsorption involving activated processes where it is likely that an energy barrier must be overcome in order to reach the adsorption geometry, and the substrate surface undergoes a significant reconstruction. In the present work, non-activated and activated adsorption may be regarded as corresponding to structures formed at low temperature and at room (or higher) temperature, respectively.

A. Adsorbate geometry

By calculating the adsorption energy for various coverages and adsorption sites, detailed insight about stable and metastable adsorbate geometries and structural phase transitions can be obtained. Furthermore, an accurate knowledge of the adsorbate and substrate atomic geometry is crucial for any additional analysis of the adsorbate properties, as for example, the surface electron density of states, chemical reactivity, and adsorbate induced work function changes. The technical details of the density functional theory calculations are given elsewhere [21,68].

The stable and metastable geometries are determined by an automated movement of the atoms of the adsorbate and substrate surface on the Born-Oppenheimer energy surface into the total energy minimum. For the analysis, it is necessary to define the *adsorption energy per adatom*. We will write this definition down using indices which refer to the adsorption of Na on Al(111), but a transformation to other systems is obvious. The adsorption energy is the difference of the total energy of the adsorbate system and the total energy of the clean, unreconstructed Al(111) substrate together with a free, neutral Na atom. Because total energies of atoms have negative values, the present and usually applied definition, associates exothermal adsorption with a positive adsorption energy [71]. The adsorption energy for the *on-surface* (non-activated) adsorption is given by

$$E_{\mathrm{ad}}^{\mathrm{Na/Al(111)}} = E^{\mathrm{Al(111)}} + E^{\mathrm{Na\text{-}atom}} - E^{\mathrm{Na/Al(111)}} \quad ,$$

(14)

where $E^{\mathrm{Na/Al(111)}}$ is the total energy per adatom of the adsorbate system, $E^{\mathrm{Al(111)}}$ is the total energy of the clean Al(111) substrate, and $E^{\mathrm{Na\text{-}atom}}$ is the total energy of a free Na atom.

For substitutional adsorption the definition is in principle identical, however, one has to take into account that the total energy $E^{\mathrm{Na/Al(111)}}$ now corresponds to a system with a substitutional Na atom for which the kicked off surface Al atom has diffused to a kink site at a step where it is rebound. Thus, for the substitutional adsorption the adsorption energy is

$$E_{\mathrm{ad}}^{\mathrm{Na/Al(111)\text{-}sub}} = E^{\mathrm{Al(111)}} + E^{\mathrm{Na\text{-}atom}} - E^{\mathrm{Na/Al(111)\text{-}sub}}$$

$$- (E^{\mathrm{Al\text{-}atom}} - E_{\mathrm{coh}}) \quad .$$

(15)

Here we have written the total energy of the displaced Al atom which is rebound at a kink site, as the sum of the total energy of the free Al atom and the negative of the cohesive energy . Thus, we assume thermal equilibrium and take into account that this is transmitted by kink sites at steps. The quantity $E^{\mathrm{Na/Al(111)\text{-}sub}}$ in equ. 15 is the total energy of the slab with the adatoms adsorbed in substitutional sites.

It is sometimes useful for a more transparent discussion to describe the substitutional adsorption in terms of two independent processes, namely, at first the creation of the surface vacancy structure, and then the chemisorption of the adatoms on the substrate surface with vacancies. Firstly, the energy required to create the surface vacancy structure is equal to the total energy of the (reconstructed) substrate (with surface vacancies), E^{vac}, plus the total energy of an atom at the kink site minus the total energy of the clean and unreconstructed surface,

$$E_f^{\mathrm{vac}} = E^{\mathrm{vac}} + (E^{\mathrm{Al\text{-}atom}} - E_{\mathrm{coh}}) - E^{\mathrm{Al(111)}} \quad . \quad (16)$$

The vacancy formation energy has typically a positive value, as it usually costs energy to create a vacancy. In the second process, the vacancies are occupied by the adatoms. This allows us to define the *binding energy* per substitutionally adsorbed adatom, E_b^{sub},

$$E_b^{\mathrm{sub}} = E_{\mathrm{ad}}^{\mathrm{Na/Al(111)\text{-}sub}} + E_f^{\mathrm{vac}} \quad . \quad (17)$$

For the on-surface adsorption the *binding* and *adsorption* energies are the same.

In general, when a surface structure is considered which has a different number of substrate atoms to the clean unreconstructed surface the required or surplus substrate atoms are taken from or to kink sites at steps, using again the fact that in thermal equilibrium kink sites represent the thermodynamic reservoir for substrate atoms and establish that the chemical potential equals the cohesive energy.

1. Atomic geometries of K on Al(111) for $0 < \Theta_{\mathrm{K}} \leq 0.33$

This subsection describes various adsorbate geometries which are assumed by potassium atoms on the (111) surface of aluminum, depending on the adsorption temperature and the adsorbate coverage. At first, non-activated adsorption is discussed, for which the calculations predict that at low coverage the adatoms form a disordered homogeneous adlayer with the potassium atoms occupying preferentially on-surface hollow sites. At $\Theta_{\mathrm{K}} \approx 0.15$ a structural phase transition occurs from this homogeneous adlayer into close-packed islands in which the adatoms occupy on-top positions. If thermal energy is available to overcome energy barriers, the adatoms in these islands undergo a site change into a substitutional geometry. Surprisingly, the surface periodicity is unchanged in this major disruption of the surface, in which one third of the surface Al atoms are removed. The subsection is concluded with a brief comparison of the DFT-LDA results with recent experimental studies.

The calculated adsorption energy for K on Al(111) for several conceivable adsorption sites and for various coverages are collected in Figs. 6a and 6b, where the latter also gives the binding energies for substitutional adsorption, E_b^{sub}, and the vacancy formation energies, E_f^{vac}.

These results show that at low coverages the on-surface threefold hollow position is energetically preferred. The rapid decrease of the adsorption energy with increasing coverage reflects a strong adsorbate-adsorbate repulsion. This is consistent with the strong adsorbate induced dipole moments which repel each other. The K atoms are expected therefore to be homogeneously distributed over the surface at low coverages. For higher coverages the results indicate that a phase transition occurs to adsorbate islands with a condensed structure of $(\sqrt{3} \times \sqrt{3})R30°$ periodicity. The local coverage in these islands is $\Theta_K = 1/3$. Interestingly, the adsorption energies for this periodicity are more favorable than those with a (2×2) periodicity and coverage $\Theta_K = 1/4$. It can be therefore concluded that for coverages smaller than $\Theta_K \approx 0.15$ the Gurney picture and the dipole-dipole repulsion (and depolarization) appear to describe the physics of the adlayer appropriately. However, when the coverage is increased, there is a crossover point, where a different mechanism becomes energetically preferable: Instead of keeping the largely ionic adsorbate-substrate bonds and the energetically unfavorable repulsive interaction between adatoms, it becomes energetically beneficial to build up a close-packed potassium layer with a metallic bonding. Together with this, a reduction of the strength of the adsorbate-substrate bonding takes place. We had noted above that this is a very general phenomenon (roughly the bond strength scales with the square root of the coordination number). Thus, with the increase of coordination, the adsorbate-substrate bond becomes weaker and longer. The calculations show that in this condensed structure with $(\sqrt{3} \times \sqrt{3})$ periodicity, the on-top position is now energetically slightly more favorable than the on-surface hollow position. Thus, for non-activated adsorption the theory predicts a structural phase transition from a homogenous, rather open adlayer with adatoms preferentially occupying the on-surface hollow sites, into two-dimensional islands with a $(\sqrt{3} \times \sqrt{3})$ structure where the adatoms occupy on-top sites. This phase transition is indicated by the dashed line in Fig. 6a.

Figure 6a shows that the adsorption energies of all the geometries considered with the $(\sqrt{3} \times \sqrt{3})R30°$ periodicity are very similar, which indicates that at room temperature substitutional adsorption becomes energetically possible. In order to reach the substitutional geometry an energy barrier must be overcome to reconstruct the substrate surface. We will at first analyze the on-surface $(\sqrt{3} \times \sqrt{3})R30°$ adlayer and then we come back to the substitutional adsorption.

For low temperature (i.e., non-activated) adsorption, Fig. 6a predicts that simultaneously with the island formation a site change occurs; the adatoms switch from on-surface hollow sites to on-top sites, which also involves a noticeable relaxation of the substrate [21,32]. In particular, the Al atoms in the first substrate layer beneath the on-top K atoms are moved down and the Al atoms, between the on-top K adatoms are shifted upwards, relative to the geometry of the unrelaxed substrate surface (see

Fig. 7a). It is important to note that the atomic radius of potassium is significantly larger than that of Al. This suggests, what is fully supported by the calculations, that K adatoms experience a rather small corrugation of the Al (111) surface. In fact, with the above-mentioned substrate relaxation, and because of the smaller K-Al bond length in the on-top geometry (due to the lower coordination of the K adatom) potassium at on-top sites come even closer to the surface than for the on-surface hollow sites. As a consequence, a better embedding of the adatoms in the substrate electron density is achieved.

In the substitutional geometry, which can be reached when thermal energy enables energy barriers to be overcome, it is found that because of the larger size of the alkali metal atoms compared to the Al atoms, the K adatoms jut out of the surface (see Fig. 7b). The effective radius of K in the substitutional site is larger than it is in the on-top site as can be seen clearly from comparing Figs. 7a and 7b. This trend reflects again the relation between the bond strength and the local coordination: the higher the coordination, the weaker each bond is, and the longer each bond length is. The DFT-LDA results [21] gives this increase in bond length as about 16%, and a LEED analysis [32] gives 19%. With respect to the interatomic distances of the on-top geometry, the nearest-neighbor K-Al distances are 3.38 and 3.23 Å, and for the substitutional site the values are 3.70 and 3.58 Å, as obtained from the DFT-LDA calculations and the LEED analysis, respectively. A rough theoretical estimate of the temperature at which the transition from on-top to substitutional adsorption could occur with a measurable rate was obtained [32] by assuming that the transition state of the reaction path is such that the K atoms are in substitutional sites and the ejected Al atoms are in isolated positions on the surface (not yet rebounded at steps). This transition state corresponds to an energy barrier of $E^b = 0.8$ eV. The Arrhenius equation, with a reasonable (but rough) estimate of the pre-exponential factor for the kick out event, then yields a transition temperature of 220 K.

The nature of the adsorbate-adsorbate interaction for the substitutional site and the mechanism actuating the island formation with a substrate reconstruction with the $(\sqrt{3} \times \sqrt{3})R30°$ structure can be learnt from Fig. 6b. It shows that the vacancy formation energy is particularly low for the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure compared to lower concentration vacancy structures. This behavior reflects an attractive vacancy-vacancy interaction, which is actuated by the fact that the group III element Al can easily assume covalent bonds. For the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure, which is equivalent to that of a graphite layer, the coordination of the surface Al adatoms indeed gives rise to the formation of directional bonds between the surface Al atoms. Figure 6b shows that the binding energy of K in a surface vacancy is relatively insensitive to the coverage and even exhibits a slight repulsive interaction between the K adatoms as indicated by the small decrease in binding

energy of the $(\sqrt{3} \times \sqrt{3})R30°$ structure as compared to the lower coverage structures. Thus it is the relative stability of the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure, which is the driving force for the island formation with a substitutional $(\sqrt{3} \times \sqrt{3})R30°$ structure [21].

Turning now to experimental studies we like to mention the low energy electron diffraction (LEED) study [32], of which some results were already noted above. This investigation clearly proved that the $(\sqrt{3} \times \sqrt{3})R30°$ structure formed at low temperature contains K atoms in the on-top site, which, on warming to room temperature transforms irreversibly into a $(\sqrt{3} \times \sqrt{3})R30°$ structure where the K atoms adsorb substitutionally. That is, even if the temperature is lowered the K atoms will remain in substitutional sites.

The two different phase transitions predicted by the theory (on-surface hollow sites → on-top site island formation, and on-surface → substitutional geometry) are also consistent with high resolution core level spectroscopy (HRCLS) measurements [48] which show that island formation starts at $\Theta_K = 0.12$ and 0.10 at low and room temperature, respectively. Similarly, a recent experimental study of the temperature dependence of optical second-harmonic generation [72] found that at coverage $\Theta_K = 0.06$ no phase transition occurred when warming to room temperature whereas at $\Theta_K = 0.12$ the transition took place. These experiments thus confirm the theoretical estimate, which was $\Theta_K \approx 0.15$, quite well. The temperature at which the phase transition into the substitutional adsorbate islands takes place was measured as 210 K [72] which is in surprising agreement with the rough theoretical estimate [32] noted above.

2. Atomic geometries of Na on Al(111) for $0 < \Theta_{Na} \leq 0.56$

For Na on Al(111) the same adsorbate geometries and coverages have been investigated by DFT-LDA calculations as for K on Al(111), with the addition of a structure with a (4×4) periodicity corresponding to coverage $\Theta_{Na} = 9/16$ which represents a densely packed hexagonal adlayer with nine Na adatoms per surface unit cell all occupying different (mostly low symmetry) on-surface sites. Furthermore, a variety of many different structures at $\Theta_{Na} = 0.5$ was analyzed, because experiments had indicated a strongly intermixed surface geometry, without, however, giving a clue about the structure. The calculations predict phase transitions which are very similar to those of K/Al(111), but some aspects are noticeably different, due to the fact that Na is smaller than potassium although still larger than Al. The $\Theta_{Na} = 0.5$ structure represents the most significant difference to the potassium adsorbate, but it is also unique with respect to any other adsorbate system: This structure may be described as an ordered four-layer surface alloy on an unreconstructed Al(111) substrate.

We start with a discussion of the theoretical results for the non-activated adsorption; they are summarized in Fig. 8a and can be described as follows: For low coverages the on-surface hollow site is energetically most favorable and, in a manner similar to that for K on Al(111), a strong repulsive adsorbate-adsorbate interaction is obvious. In this case, as opposed to K on Al(111) the on-top site is *significantly* less favorable than the on-surface hollow site at all coverages considered. This can be attributed to the smaller size of the Na atoms which experience a more highly corrugated potential energy surface due to the substrate atomic structure than the larger K atoms. Figure 8a shows that the condensed structure (the atomic geometry is displayed in Fig. 9a) for $\Theta_{Na} = 9/16$ is energetically more favorable than homogeneous adlayers of Na for coverages larger than approximately $\Theta_{Na} = 0.1$. Accordingly, these results imply that for very low coverages the adsorbates occupy on-surface hollow sites and are uniformly distributed over the surface (homogeneous adlayers) but for coverages greater than about $\Theta_{Na} = 0.1$, island formation with the condensed structure and a (4×4) periodicity occurs as indicated by the dashed line. This is explained in much the same way as was done in the discussion of the condensation-into-islands phenomenon in Section IV A 1 for K/Al(111).

The theoretical results corresponding to activated adsorption are collected in Fig. 8b where for Na in the substitutional geometry the adsorption, binding, and vacancy formation energies are displayed. It can be seen that the adsorption energy for the substitutional geometry is the most favorable for *all* coverages investigated. In particular, substitutional adsorption with a $(\sqrt{3} \times \sqrt{3})R30°$ periodicity has *the* most favorable adsorption energy. It is therefore expected that a condensation into $(\sqrt{3} \times \sqrt{3})R30°$ islands with the Na atoms in substitutional sites occurs, beginning at very low coverages, provided that thermal energy enables the transition to occur. The atomic geometry is depicted in Fig. 9b; it is equivalent to that of Fig. 7b with the only difference being the sizes of the adatoms. The mechanism which stabilizes the $(\sqrt{3} \times \sqrt{3})R30°$ structure of the substitutional adsorption is identified as being the same as that for K on Al(111) [31], i.e., as being due to the particular stability of the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure.

Upon further deposition of Na at room temperature onto the $(\sqrt{3} \times \sqrt{3})R30°$ substitutional adsorbate structure, the formation of a (2×2) surface structure has been observed experimentally. This phase corresponds to a coverage of $\Theta_{Na} = 1/2$ where there are two Na atoms in the surface unit cell. It has been the subject of a number of studies, and many different models have been proposed. Initially it was suggested that the structure corresponds to three domains of (2×1) periodicity, involving Na atoms adsorbed on an unreconstructed substrate [73]. Subsequently it was argued that the structure consists of two layers of Na atoms, each with (2×2) periodicity, located on an unreconstructed substrate [46]. Re-

cent studies using HRCLS [49], normal incidence standing x-ray wave-field (NISXW) and surface extended x-ray adsorption fine structure (SEXAFS) [50] have surprisingly shown that a strong intermixing of the Na and Al atoms in the surface region occurs. In the NISXW study a model was proposed involving two reconstructed layers each of stoichiometry $NaAl_2$ while from a recent scanning tunnel microscopy (STM) study [74,75] it was suggested that the (2×2) phase consists of two Na layers where one Na adatom in the surface unit cell is located in a surface substitutional site and the second Na atom occupies an on-surface hollow site. In order to clarify the situation regarding the exact surface atomic structure of this controversial phase, DFT-LDA calculations were carried out for a large number of conceivable geometries [51]. These calculations provided evidence for the uniqueness of the structure and permitted the rejection of all of the above-mentioned suggested models. The identified structure is significantly more complex and unexpected than any of the alkali metal adsorption systems studied so far. It is drawn in Fig. 9c and may be described as a composite double layer ordered surface alloy and has the lowest total energy. In this structure an Al atom is incorporated into a double Na layer of which one of the Na atoms in the surface unit cell occupies a substitutional site and the second Na atom plus an Al atom are situated in fcc- and hcp-hollow sites, respectively. Alternatively, it could be described as a four layer Al-Na-Al-Na alloy on an unreconstructed $Al(111)$ surface.

Intuitively one might expect that the Al atom in the composite double layer would adsorb in the fcc-hollow site rather than in the hcp-hollow site (continuing growth of the bulk), and that the Na atom would assume the hcp-hollow site. It has been shown from the calculations that the reason this does not occur is due to a larger relaxation of the reconstructed Al layer (the Al layer containing three Al atoms per surface unit cell) and of the substrate, compared to the structure where the atoms occupy the opposite hollow sites. These relaxations correspond to a significant energy gain of 0.12 eV per surface unit cell.

The adsorption energy per Na atom in this surface alloy structure is less than that of the $(\sqrt{3} \times \sqrt{3})R30°$ substitutional phase and greater than that of the non-activated (4×4) surface geometry. The fact that it is greater than the (4×4) structure explains why the (4×4) structure is not found at room temperature. The result that the (2×2) surface alloy structure has a smaller adsorption energy than the substitutional adsorbate $(\sqrt{3} \times \sqrt{3})R30°$ structure, implies that the (2×2) surface alloy will only form when it is not possible for the $(\sqrt{3} \times \sqrt{3})R30°$ structure to grow any further.

From consideration of the atomic structure of the (2×2) phase, it would seem that no mass transport is necessary in its formation. However, the lower coverage $(\sqrt{3} \times \sqrt{3})R30°$ substitutional structure involves displacement of 1/3 of a monolayer of Al atoms, which are assumed to diffuse across the surface to be re-adsorbed at steps. That is, the steps act as *sinks* for the displaced substrate atoms. The results indicate, therefore, that formation of the (2×2) structure from the $(\sqrt{3} \times \sqrt{3})R30°$ structure involves the reverse process, that is, diffusion of 1/3 of a monolayer of Al atoms back from the steps which are used in the formation of the (2×2) structure. In this case the steps serve as *sources* of substrate atoms [52].

We note that the direct involvement of steps is one, but not the only possibility. Another mechanism could be that the kicked out Na atoms diffuse to regions between on-surface hollow-site Na atoms. This mechanism gives rise simultaneously to two domains of substitutional adsorption, one on the lower terrace from where the Al atom was ejected and one on the upper terrace to where the ejected Al atom finally resides. This two-domain mechanism has been discussed for the Na adsorption on the $Al(100)$ surface [38].

It is appropriate to briefly mention some of the recent experimental studies. The results of the calculations for non-activated adsorption are compatible with a SEXAFS study of the (4×4) structure formed at low temperature which found that the Na atoms form a quasi-hexagonal close-packed adlayer where, within the unit cell, there is a slight clustering and rotation of the Na adatoms with respect to a strictly hexagonal close-packed arrangement [76]. In the calculations these small displacements of the Na atoms within the (4×4) hexagonal adlayer were not considered. For activated adsorption the results of the DFT-LDA calculations are in full accordance with SEXAFS [20], LEED [35], and NISXW [30] studies of the $(\sqrt{3} \times \sqrt{3})R30°$ phase. Nearest neighbor Na-Al distances in the substitutional geometry of 3.13, 3.21, 3.31, and 3.09 Å were determined from the DFT-LDA calculations, LEED intensity, SEXAFS, and NISXW studies, respectively. The theoretical results are also in accordance with STM pictures taken at room temperature in the coverage range below $\Theta_{Na} = 1/2$, which showed that islands with a $(\sqrt{3} \times \sqrt{3})R30°$ structure are present at low coverages and increase in size with coverage up to $\Theta_{Na} = 1/3$. The ordering of the total energies of the $(\sqrt{3} \times \sqrt{3})R30°$ substitutional structure and the (2×2) four-layer surface alloy structure is consistent with an STM study [74,75] which shows that initially islands with a $(\sqrt{3} \times \sqrt{3})R30°$ structure form rather than with a (2×2) structure.

The complex structure of the four-layer surface alloy proposed in the DFT-LDA study has been confirmed by a detailed LEED intensity analysis [52]. SEXAFS data are consistent with the surface structure but the analysis does not allow a unique discrimination against alternative models [52]. In addition, results of an x-ray photoelectron diffraction (XPD) study [77] also agree with the predicted structure. For the first three interlayer spacings the values determined by DFT-LDA, LEED, SEXAFS, and XPD agree to within 0.13 Å [78]. The DFT-LDA and LEED results show, in particular, remarkable agreement. Both identify the presence of small (≈ 0.04 Å) lateral displacements of the Al atoms in layers four and

five and small vertical displacements of the Al atoms in layers five and six (counting the uppermost Na layer as the first, see Fig. 9c). The structure derived from the DFT-LDA total energy minimization is at variance with that suggested by the STM analysis of Brune *et al.* [74,75] which is apparently due to the fact that STM is unable to detect all surface atoms with equal clarity and to identify the atomic species unambiguously.

3. Atomic geometries of Na on Al (001) for $0 < \Theta_{Na} \leq 0.5$

The atomic density of the fcc (001) surface is about 15% lower than that of the (111) surface, and the (001) surface therefore has higher diffusion energy barriers to adatoms. As a consequence it is to be expected that the behavior of adsorbates on the (001) surface may exhibit some differences to on the (111) surface. We will show and explain in this subsection that at low temperatures Na adatoms always occupy on-surface hollow sites with a repulsive intra layer interaction and no indication of a phase transition (at low coverage) into close-packed islands. At higher temperature we find that Na adatoms occupy at low coverage also on-surface hollow sites, but at $\Theta_{Na} \approx 0.15$ a transition into islands with a substitutional geometry and a $c(2 \times 2)$ periodicity is predicted. In contrast to the other sections, we will discuss at greater length the results of recent experiments because the experimental situation and published conclusions are more complex and contradictory than those for the other systems.

DFT-LDA calculations were carried out for many possible surface geometries and coverages [36,37] and some of these results are shown in Fig. 10a.

We start with a discussion of the on-surface geometries which are relevant for non-activated adsorption. The energies of different on-surface sites differ more widely than those for Na on Al (111) which can be attributed to the more corrugated potential energy surface of Al (001). For the $c(2 \times 2)$ structure ($\Theta_{Na} = 0.5$) the adsorption energies for the on-top, bridge, and on-surface hollow sites are 1.33, 1.45, and 1.59 eV [36]. Therefore, only the on-surface hollow sites were considered further, the other sites were regarded as unlikely in the considered coverage range. Figure 10a shows that the on-surface hollow site is clearly preferred over the substitutional site at low coverages. Its adsorption energy rapidly decreases with increasing coverage, similar to K and Na on Al (111), indicating a strong repulsive interaction between the Na atoms. However, differently to the adsorption on the (111) surface, the theoretical results for Na on Al (001) give no indication that a condensation into close-packed islands takes place. This is quite certain for low coverage, but for $\Theta > 0.3$ we would not rule out that a phase transition into $\Theta = 0.5$ condensed islands can occur. Figure 10a suggests that the adlayer is compressed gradually up to a coverage of $\Theta_{Na} = 0.5$ for which Fig. 11a

displays the structure. The difference to the Al (111) surface arises because the adsorbate-substrate bonding is stronger on Al (001) due to the better embedding of the Na atom when occupying the more open on-surface hollow site. It therefore remains energetically advantageous to keep those strong bonds with the substrate rather than to build up metallic bonds in a condensed adlayer island.

Figure 10a also contains the results relevant for activated adsorption, namely the adsorption energies of substitutional geometries. It can be seen that the adsorption energy for Na in the surface substitutional site depends much more weakly on coverage than that for the on-surface Na, and in fact, the adsorption energy for the $c(2 \times 2)$ substitutional structure, which is displayed in Fig. 11b, is more favorable than that of the lower coverage substitutional structures. These results are interpreted as follows: At low coverages the on-surface adsorption in a homogeneous adlayer is the stable structure for low as well as high temperature, but for higher coverages on-surface adsorption becomes metastable. For high temperature adsorption the adatoms then switch to substitutional sites, forming islands with a $c(2 \times 2)$ structure (see Fig. 11b) which increase in size with increasing coverage. The phase transition from the on-surface hollow site to substitutional adsorption is indicated in Fig. 10a by the dashed line.

The shape of the adsorption energy versus coverage curve for Na in the substitutional site (E_{ad}^{sub} in Fig. 10b) appears, at first glance, somewhat similar to the result for K and Na on Al (111) (see Figs. 6b and 8b). However, from a plot of the adsorption, binding, and vacancy formation energies, which are also shown Fig. 10b, it can be seen that even though the *adsorption energy* versus coverage curve exhibits the same trend as for K and Na on Al (111), that is, in both cases the most favorable adsorption energy is obtained for the highest coverage structure, the constituent components, namely, the binding and vacancy formation energies comply to a different behavior. We see that on the (001) surface the binding energy is particularly favorable for the $c(2 \times 2)$ structure, reflecting an *attractive* adsorbate-adsorbate interaction which actuates island formation. It can be seen in addition that the surface vacancy formation energy shows *little* dependence on surface vacancy concentration.

An additional surface structure was considered in the DFT-LDA calculations, corresponding to coverage $\Theta = 0.5$ which contains Na atoms in on-surface hollow and in substitutional sites [37]. The surface unit cell used was twice that of the $c(2 \times 2)$ cell, i.e., $(\sqrt{2} \times 2\sqrt{2})R45°$. In this arrangement the Na atoms form a quasi-hexagonal structure, which could also be described as alternating strips of Na atoms in on-surface hollow and substitutional sites. It was found that the adsorption energy of this structure is between that of the on-surface hollow and substitutional sites. Accordingly, similar mixed hollow-substitutional geometries may well be present in the temperature and coverage ranges at which the phase transi-

tion takes place, and they may also exist as metastable surface geometries.

We now turn to a brief discussion of experimental studies. Early LEED intensity analyses [79,80] of $c(2 \times 2)$ Na/Al(001) concluded that the adatoms occupy the on-surface hollow site. In the preparation of the surface from which the intensity versus energy curves were measured the sample was annealed at 360 K. Recent experimental results are, however, at variance with this conclusion. HRCLS [81] and SEXAFS [82] studies demonstrated convincingly that the atomic structure of the $c(2 \times 2)$ phases are different when formed at low temperature and at room temperature, that the structural phase transition is irreversible, and that the room temperature structure is due to a mixing of Na and Al atoms. The SEXAFS study determined the on-surface hollow site as the adsorption site at low temperature and for the structure formed at room temperature three possible models were proposed with one being favored which consists of Na atoms in on-top sites beneath a $c(2 \times 2)$ Al layer where the Al atoms are adsorbed in hollow sites with respect to the Na adlayer. The DFT-LDA analysis of these three surface alloy structures showed that they are energetically very unfavorable, and these structures have therefore been indubitably rejected [37]. Thus, these experimental results for the low temperature adsorption agree with the DFT-LDA results of Fig. 11a. Also the experimental evidence for a phase transition towards an intermixed structure agrees with the theoretical prediction. However, the geometry which was derived from the SEXAFS analysis is at clear variance with the DFT-LDA result shown in Fig. 11b. Interestingly, in an XPD study [39,77] of the room temperature $c(2 \times 2)$ phase of Na on Al(001) it was concluded that the surface may contain two domains, one with Na atoms in the substitutional site (45% occupancy) and the other with the Na atoms still in the on-surface hollow sites (55% occupancy).

A recent dynamical LEED intensity analysis [38] shows that the low temperature $c(2 \times 2)$ phase contains Na in on-surface hollow sites and in the room temperature $c(2 \times 2)$ phase the Na atoms adsorb substitutionally, in very good agreement with the DFT-LDA calculations. Importantly, the LEED study reveals that the transition from on-surface hollow sites to substitutional sites proceeds in a gradual step-by-step way, beginning at a temperature of approximately 180 K, and that on completion of the phase transition (determined to occur at about 260 K) the contribution to the LEED intensities from substitutional adsorption is not less than 90%.

As discussed in Ref. [38], one particular atomic configuration consistent with the behavior of the temperature dependent satellite features, which are seen during the phase transition, is one which corresponds to the creation of domains arranged in narrow rows or "strips" where the Na atoms are in substitutional sites. As the temperature is increased and the phase transition proceeds, the rows or strips of Na atoms in substitutional sites become progressively wider until at the end of the transition all adatoms are in substitutional sites, recovering again the sharp $c(2 \times 2)$ LEED pattern [38]. Three possible mechanisms are envisaged by which the substitutional geometry could be realized: i) The Na atoms cause the ejection of substrate Al atoms which diffuse across the surface to steps – the steps acting as sinks. ii) Steps on the surface act as sources of Al atoms which diffuse to the regions between the on-surface hollow-site Na atoms, forming exactly the substitutional geometry. iii) As in i) where the Na atoms eject substrate Al atoms which, however, do not move to steps but diffuse as in ii) to the regions between on-surface hollow-site Na atoms. The latter mechanism gives rise simultaneously to two regions of substitutional adsorption, one on the "lower" terrace from where the Al atom was ejected and one on an "upper" terrace to where the ejected Al atom finally resides. "Kick-out" of the Al atoms by the Na atoms could proceed in a "chain-reaction-like" process which would give rise to the formation of rows or strips of Na atoms in substitutional sites, either on one terrace only if process i) occurs or on two terraces if process iii) occurs. The starting point for the "kick-out" process could conceivably occur at imperfections or steps on the surface.

The interatomic distances obtained by the various experiments are in good agreement with those obtained from the DFT-LDA calculations. For the on-surface hollow site, the obtained values read 3.08, 3.21, 2.93, 3.27 Å as obtained by the DFT-LDA, SEXAFS, XPD, and LEED studies. For the room temperature phase the Na-Al bond lengths determined by the DFT-LDA, XPD, and LEED investigations are 3.02, 3.11, and 3.07 Å respectively. For the substitutional site, DFT-LDA and LEED identify a small (≈ 0.05 Å) vertical displacement of the Al atoms in the second Al layer. Both studies also find that the effective radius of Na in the substitutional site is shorter than in the on-surface hollow site: approximately 4% from DFT-LDA and 11% from LEED.

In a manner similar to that described above for K on Al, the temperature for the on-surface hollow–to–surface substitutional transition has been estimated from DFT-LDA calculations. The value obtained was 180 K and calculated by assuming that the transition state of the reaction path is such that the Na atoms are in substitutional sites and the ejected Al atoms are in the energetically least favorable position of the exchange diffusion mechanism (two Al atoms above a surface vacancy, see Refs. [83,84]), not yet rebounded at kink sites at steps. This rough theoretical estimate of the transition temperature is in good agreement with the value of 160 K determined from the HRCLS study [81] and with 180 K as determined in the LEED study [38].

B. Adsorbate bonding and electronic properties

The widely differing adsorbate geometries and their strong dependencies on coverage and temperature, as de-

scribed in the previous section, go together with significant changes of the surface chemical bond and surface electronic structure. In this respect, in this section, we discuss the adsorbate-substrate and adsorbate-adsorbate interaction of the different surface structures, the associated electron densities at the surface, and the resulting work function changes.

As mentioned in the introduction, the characteristic change in the work function with coverage, $\Delta\Phi(\Theta)$, is typically explained in terms of the Gurney picture and the "usual form" (see Fig. 2) can be described reasonably well within a model in which a high r_s jellium is adsorbed on $r_s = 2$ jellium. Alternatively, but with essentially the same conclusions, Muscat and Newns [7,8] examined the coverage dependence of the adsorbate-substrate and adsorbate-adsorbate interaction using an empirical Anderson-type Hamiltonian [85,86], which takes the alkali metal valence states and the eigenstates of the semi-infinite substrate properly into account. They studied the work function change for alkali metal atoms on transition metal surfaces [8].

To obtain *quantitative* agreement between calculated and experimental results it is necessary to take into account in the calculations that the atomic geometry (of adsorbate and substrate) and the surface electronic structure are closely linked. Thus, a realistic description of the surface electronic properties necessarily requires a correct treatment of the various adsorbate arrangements discussed in Section IV A above. To highlight this point we investigate the effect on the calculated adsorbate induced change of the work function by assuming hypothetical atomic arrangements of Na on Al (111) where the Na adatoms are homogeneously distributed over the surface for the specified coverage. The self-consistently calculated surface dipole moments and work function change corresponding to these structures are shown in Figs. 12a and 12b, respectively. In agreement with the traditional picture of alkali metal adsorption, there is a significant decrease of the surface dipole moment with increasing coverage. For comparison, the results for homogeneous adlayers of Na in the substitutional site are also shown. Here we see that the depolarization effect, which is one indicator of the strength of the adatom-adatom interaction, is much less dramatic. This is due to the fact that in the substitutional site the Na atoms sit lower in the surface and the repulsive adsorbate-adsorbate interaction is screened better. As a consequence of the lower (closer to the substrate) position of the substitutional adsorbate we also see that the dipole moment (at low coverage) is much smaller – largely due to the smaller dipole length. As a consequence of this better screening of the adsorbate-adsorbate interaction for substitutional adsorption, i.e., the (near) absence of depolarization, the $\Delta\Phi(\Theta)$ curve for the homogeneous substitutionally adsorbed adlayer does not exhibit a minimum. The obtained work function change in Fig. 12b agrees reasonably well, as expected, with that of Lang's jellium on jellium calculation. However, as we will discuss below, the curves for Fig. 2 and 12b are in clear disagreement with the measured results.

1. K on Al (111)

The calculated change in work function of potassium on Al (111) corresponding to the realistic atomic arrangements, which were discussed in Section IV A 1, are displayed in Figs. 13a and 13b for non-activated and activated adsorption, respectively. For the non-activated adsorption the adatoms stay on the surface, but at $\Theta \approx 0.15$ they change from a homogeneous adlayer to close-packed islands (the structure was shown in Fig. 7a), which for increasing coverage increase in size. This phase transition is the reason for the minimum in the dashed curve of Fig. 13a. The comparison with the low temperature experimental result shows reasonable agreement. In particular we emphasize that the origin of the minimum in $\Delta\Phi(\Theta)$ is not due to the adsorbate-adsorbate depolarization, but to the phase transition into close-packed islands. It is interesting to inspect the adsorbate-induced change of the electron density (see Fig. 14a). Within this structure, the adsorbate-adsorbate distance is only 5% larger than that of bulk K, and Fig. 14a indeed reveals that there is considerable charge density between the K adatoms. We therefore tend to classify the bonding within the adlayer as metallic. Consistent with this we note that the surface band structure of this adlayer is similar to that of a free-standing $(\sqrt{3} \times \sqrt{3})R30°$-K layer [87].

The calculated work function change for activated adsorption is shown in Fig. 13b. Although this curve looks similar to that of the low temperature (non-activated) adsorption, this similarity is in fact highly incidental. The physics behind the curve of Fig. 13b is that of a structural phase transition at $\Theta \approx 0.15$ into islands with substitutional adatoms (compare Fig. 7b). Incidentally, this phase transition occurs at about the same coverage as the phase transition of the non-activated adsorption which implies that the minima of the $\Delta\Phi(\Theta)$ curves of Figs. 13a and 13b are at about the same positions. The charge density between the adsorbates (see Fig. 14b), which is essentially provided by the substrate atoms, is significant and screens the adsorbate-adsorbate interaction quite efficiently. Therefore the substitutionally adsorbed potassium can attain its ionic character even in the close-packed $(\sqrt{3} \times \sqrt{3})R30°$ structure in clear contrast to the on-surface adsorbate structures. The DOS for the substitutional adsorbate (not shown) is also significantly different to that of the on-surface adsorbate structure, and it is mainly due to the reconstruction of the Al substrate, i.e., to the removal of one third of all surface atoms; the K atoms which occupy the surface vacancies modify the vacancy electronic structure only little [87].

13

The behavior of Na on Al (111) is qualitatively similar to that of K on Al (111). However, because of the smaller size of the Na atom, the condensed structure of the non-activated adsorption is more dense for Na than for K. The (4×4) structure of the Na islands (local coverage $\Theta = 9/16$), which is assumed for low temperature adsorption and coverages above $\Theta \approx 0.1$ was displayed in Fig. 9a. The calculated work function change is shown in Fig. 15 for different temperatures. The minimum at $\Theta \approx 0.1$ marks the phase transition from the homogeneous adlayer to the condensed islands which grow in size with increasing coverage. Again we emphasize that the shape of the $\Delta\Phi(\Theta)$ curve and the physics behind this shape is significantly different to that of the "traditional" picture of Figs. 2 and 12b. In the condensed structure the nearest-neighbor Na-Na distance is very similar to that in bulk Na and the intra layer bonding can be described as metallic.

The calculated work function change with coverage for the activated adsorption follows a linear relation between $\Delta\Phi$ and Θ (see Fig. 15b). This results, because at high temperature island formation starts at very low coverage and thus the work function change is mainly determined by the surface dipole moment of the condensed $(\sqrt{3} \times \sqrt{3})R30°$-Na substitutional structure times the number of Na atoms in these islands. The work function decreases up to the point where the whole surface is covered with $(\sqrt{3} \times \sqrt{3})R30°$ substitutional Na atoms. For coverages higher than $\Theta = 1/3$ (compare Section IV A 2) a major restructuring of the surface takes place. The analysis of the work function shows that $\Delta\Phi(\Theta)$ should exhibit a minimum at $\Theta = 1/3$ ($\Delta\Phi \approx -1.6$ eV) and then increase up to $\Delta\Phi(\Theta) = -1.16$ eV at $\Theta = 1/2$ for the four-layer surface alloy. For even higher coverages the curve should reach the value of the work function of a Na crystal surface.

Similar to that of K in the substitutional site, the bonding of Na in the $(\sqrt{3} \times \sqrt{3})R30°$ substitutional structure can be described as partially ionic. The density difference plot is shown in Fig. 16.

On further deposition of one sixth of a monolayer of Na onto the substitutional $(\sqrt{3} \times \sqrt{3})R30°$-Na surface, the (2×2) surface alloy structure forms. The adsorbate induced electron density is shown in Fig. 17. Two regions of charge density maxima occur. Both are weighted towards the uppermost Al atom. Inspection of the *total* charge density reveals that the Al atom in the hcp-hollow site forms covalent-like bonds with the three Al atoms under it. This is possible because the Al atoms in the reconstructed layer underneath are rather lowly coordinated due to the displacement of one quarter of a monolayer of Al atoms. The Al-Al bondlength is shorter than in bulk Al, compare 2.66 to 2.81 Å (theoretical bulk value) reflecting the stronger and lower coordinated bonding. The *occupied* adsorbate induced DOS for the (2×2) structure

is largely determined by the Al structure, which corresponds to the Al (111) surface with $\Theta = 1/4$ vacancies plus $\Theta = 1/4$ Al atoms in the on-surface hcp-hollow sites (compare Fig. 9c). In particular we noted a peak at approximately 2 eV below the Fermi level (see Ref. [51]).

3. Na on Al (001)

Considering now Na on Al (001), we see that from inspection of the *total* charge density for the $c(2 \times 2)$ structure with Na adsorbed substitutionally, that directional bonds are formed between Al atoms of the uppermost layer (from which $\Theta = 0.5$ Al atoms have been removed) and their four nearest-neighbor atoms in the layer underneath. The density difference plot in Fig. 18 clearly displays a maximum of charge density located above the uppermost Al atoms. From inspection of the adsorbate induced DOS, an occupied and an unoccupied feature at about 2 eV below and 1 eV above the Fermi level, respectively are identified. While the peak below the Fermi level is largely due to the Al structure (substrate with vacancies), the peak above the Fermi level arises from the Na atoms. An analysis of the wave functions of these states indicated that (at least at $\overline{\Gamma}$) the occupied state is localized above the uppermost Al atoms and the unoccupied state is localized above the Na atoms.

V. CONCLUSION

In the present paper we discussed results of recent density functional theory calculations for alkali metal adsorbates on close-packed metal surfaces. The analyses support the traditional charge transfer picture of alkali metal adsorption as being an appropriate description in the limit of low coverage and non-activated adsorption, i.e., when isolated alkali metal adatoms occupy on-surface positions. It is emphasized, however, that low coverage means *very* low because adsorbate-adsorbate interactions can become very noticeable already at surprisingly low coverages (e.g. $\Theta < 0.1$) and the traditional picture, thus, should not be generally applied in the higher coverage regime. In particular we stressed the interplay of the electronic properties of the surface, which is for example reflected in the work function, and the adsorbate site.

The transition region from the regime at very low coverages, governed by electrostatic repulsion, to higher coverage regimes where adlayer phases develop which possess a cohesive interaction between the adatoms (or vacancies) is particularly interesting. In this respect, it has been shown that with increasing coverage, Na and K adsorbates on close-packed Al surfaces exhibit an unexpected variety of physical and chemical phenomena. For non-activated adsorption these phenomena include site changes and on-surface condensation phase transitions and for activated adsorption, condensation phase

transitions involving substitutional adsorption, as well as surface alloy formation. Such unusual and varied behavior as described in the present work with respect to the knowledge of several years ago, emphasizes a new updated view of alkali metal adsorption on metal surfaces.

The novel adsorption geometries were observed so far for the two close packed aluminum surfaces: Al (111) and Al (100). Thus, the metal, which so far was assumed to be the most jellium-like system, reveals in fact quite clearly the influence of its atomic structure and tendency towards geometries which are stabilized by the formation of partially covalent bonds. At this point it is not clear, whether similar behavior ought to be expected for other systems. Calculations of the formation energy of surface vacancies [88] indicate that silver and maybe also copper are further candidates for substrates where substitutional adsorption might occur. In fact, substitutional adsorption is a much more general phenomenon than hitherto expected. Atoms which are immiscible with the bulk may well intermix at the surface, because there the size mismatch can be easy accounted for by relaxations.

[1] R. W.Gurney, Phys. Rev. **47**, 479 (1935).

[2] N. D. Lang, Phys. Rev. B **4**, 4234 (1971).

[3] N. D. Lang, Solid State Phys. **28**, 225 (1973).

[4] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **34**, 531 (1975).

[5] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 212 (1976).

[6] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

[7] J. P. Muscat and D. M. Newns, Prog. in Surf. Sci. **9**, 1 (1978) and references therein.

[8] J. P. Muscat and D. M. Newns, J. Phys. C **7**, 2630 (1974).

[9] A. R. Williams and U. von Barth, in *Theory of the Inhomogeneous Electron Gas*, eds. S. Lundqvist and N. H. March (Plenum Press, New York and London, 1983).

[10] N. D. Lang, in *Theory of the Inhomogeneous Electron Gas*, eds. S. Lundqvist and N. H. March (Plenum Press, New York and London, 1983).

[11] J. W. Döbereiner, *Zur Chemie des Platins in wissenschaftlicher und technischer Beziehung* (Balz'sche Buchhandlung, Stuttgart, 1836).

[12] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

[13] A. G. Naumovets, in *The Chemical Physics of Solid Surfaces (Vol. 7): phase transitions and adsorbate restructuring at metal surfaces*, eds. D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1994).

[14] G. Ertl, Catal. Rev.-Sci. Eng. **21**, 201 (1980).

[15] W. D. Mross, Catal. Rev.-Sci. Eng. **25**, 591 (1983).

[16] T. Aruga and Y. Murata, Prog. in Surf. Sci. **31**, 61 (1989).

[17] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

[18] We note that the jellium model has also some severe limitations, as for example a negative surface energy for most metals (i.e., a density parameter $r_s \lesssim 2.5$ bohr).

[19] *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[20] A. Schmalz, S. Aminpirooz, L. Becker, J. Haase, J. Neugebauer, M. Scheffler, D. R. Batchelor, D. L. Adams, and E. Bøgh, Phys. Rev. Lett. **67**, 2163 (1991).

[21] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992).

[22] S. Lindgren, L. Walldén, J. Rundgren, P. Westrin, and J. Neve, Phys. Rev. B **28**, 6707 (1983).

[23] D. Fisher, S. Chandavarkar, I. R. Collins, R. Diehl, P. Kaukasoina and M. Lindroos, Phys. Rev. Lett. **68**, 2786 (1992); P. Kaukasonia, M. Lindroos, R. D. Diehl, D. Fisher, S. Chandavarkar, and I. R. Collins, J. Phys.: Condens. Matter **5**, 2875 (1993).

[24] D. L. Adler, I. R. Collins, X. Liang, S. J. Murray, G. S. Leatherman, K. -D. Tsuei, E. E. Chaban, S. Chandavarkar, R. McGrath, R. D. Diehl, and P. H. Citrin, Phys. Rev. B **48**, 17445 (1993).

[25] X. Shi, C. Su, D. Heskett, L. Berman, C. C. Kao, and M. J. Bedzyk, Phys. Rev. B **49**, 14638 (1994).

[26] R. Davis, X. Xu, D. P. Woodruff, K. Weiss, R. Dippel, K. Schindler, P. Hofmann, V. Fritzsche, and A. M. Bradshaw, Surf. Sci. **307/309**, 632 (1994).

[27] X. Huang, L. Q. Wang, A. E. S. von Wittenau, Z. Hussain, and D. A. Shirley, Phys. Rev. B **47**, 13626 (1993).

[28] A. V. de Carvalho, D. P. Woodruff, and M. Kerkar, Surf. Sci. **320**, 315 (1994).

[29] H. Over, H. Bludau, M. Skottke-Klein, G. Ertl, W. Moritz, and C. T. Campbell, Phys. Rev. B **45**, 8638 (1992).

[30] M. Kerkar, D. Fisher, D. P. Woodruff, R. Jones, R. Diehl, C. McConville, and B. Cowie, Phys. Rev. Lett. **68**, 3204 (1992).

[31] J. Neugebauer and M. Scheffler, Phys. Rev. Lett. **71**, 577 (1993).

[32] C. Stampfl, M. Scheffler, H. Over, J. Burchhardt, M. Nielsen, D. L. Adams and W. Moritz, Phys. Rev. Lett. **69**, 1532 (1992); Phys. Rev. B **49**, 4959 (1994); Surf. Sci. **287/288**, 418 (1993).

[33] M. M. Nielsen, J. Burchhardt, D. L. Adams, E. Lundgren, and J. N. Andersen, Phys. Rev. Lett. **72**, 3370 (1994).

[34] G. Scragg, B. C. C. Cowie, M. Kerkar, D. P. Woodruff, A. Daimellah, S. Turton, and R. G. Jones, J. Phys.: Condens. Matter **6**, 1869 (1994).

[35] M. M. Nielsen, J. Burchhardt, D. L. Adams, E. Lundgren, and J. N. Andersen, Phys. Rev. B **50**, 4718 (1994).

[36] C. Stampfl, J. Neugebauer, and M. Scheffler, Surf. Sci. **307/309**, 8 (1994).

[37] C. Stampfl, J. Neugebauer, and M. Scheffler, Surf. Reviews and Lett. **1**, 213 (1994).

[38] W. Berndt, D. Weick, C. Stampfl, A. M. Bradshaw, and M. Scheffler, submitted to Surf. Sci.

[39] R. Fasel, P. Aebi, J. Osterwalder, L. Schlapbach, R. G. Agostino, and G. Chiarello, Phys. Rev. B **50**, 14516 (1994).

[40] M. Gierer, H. Bludau, T. Hertel, H. Over, W. Moritz,

and G. Ertl, Surf. Sci. **279**, L170 (1992).

[41] T. Hertel, H. Over, H. Bludau, M. Gierer, and G. Ertl, Surf. Sci. **301**, 1 (1994).

[42] T. Hertel, H. Over, H. Bludau, M. Gierer, and G. Ertl, Phys. Rev. B **50**, 8126 (1995).

[43] H. Over, H. Bludau, M. Gierer, and G. Ertl, Surf. Rev. and Lett. this issue (1995).

[44] A. G. Naumovets, Sov. Sci. Rev. A Phys. **5**, 443 (1984).

[45] S. Modesti, C. T. Chen, Y. Ma, G. Meigs, P. Rudolf, and F. Sette, Phys. Rev. B **42**, 5381 (1990).

[46] A. Hohlfeld and K. Horn, Surf. Sci. **211/212**, 844 (1989).

[47] T. Aruga, H. Tochihara, and Y. Murata, Surf. Sci. **175**, L725 (1986).

[48] J. N. Andersen, E. Lundgren, R. Nyholm and M. Qvarford, Surf. Sci. **289**, 307 (1993).

[49] J. N. Andersen, M. Qvarford, R. Nyholm, J. F. van Acker, and E. Lundgren, Phys. Rev. Lett. **68**, 94 (1992).

[50] M. Kerkar, D. Fisher, D. P. Woodruff, R. G. Jones, R. D. Diehl and B. Cowie, Surf. Sci. **278**, 246 (1992).

[51] C. Stampfl and M. Scheffler, Surf. Sci. **319**, L23 (1994).

[52] J. Burchhardt, M. M. Nielsen, D. L. Adams, E. Lundgren, J. N. Andersen, C. Stampfl, M. Scheffler, A. Schmalz, S. Aminpirooz, and J. Haase, Phys. Rev. Lett. **xx**, yy (1995).

[53] G. A. Somorjai and M. A. Van Hove, Prog. Surf. Sci. **30**, 201 (1989).

[54] C. J. Barnes, in *The Chemical Physics of Solid Surfaces (Vol. 7): phase transitions and adsorbate restructuring at metal surfaces*, eds. D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1994).

[55] R. J. Behm, in *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[56] V. Heine and D. Marks, Surf. Sci. **115**, 65 (1986).

[57] H. Ishida, Phys. Rev. B **38**, 8006 (1988).

[58] H. Ishida, Phys. Rev. B **42**, 10899 (1990).

[59] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **64**, 571 (1990).

[60] M. Scheffler, Ch. Droste, A. Fleszar, F. Máca, G. Wachutka and G. Barzel, Physica B **172**, 143 (1991).

[61] J. Bormet, J. Neugebauer, and M. Scheffler, Phys. Rev. B **49**, 17242 (1994).

[62] L. Yang, G. Vielsack, and M. Scheffler, to be published.

[63] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[64] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[65] L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).

[66] J. Bormet, B. Wenzien, J. Neugebauer, and M. Scheffler, Computer Phys. Commun. **79**, 124 (1994).

[67] K. Kambe and M. Scheffler, Surf. Sci. **89**, 262 (1979); F. Máca and M. Scheffler, Comp. Phys. Commun. **51**, 381 (1988); J. Bormet, B. Wenzien, and M. Scheffler, Computer Phys. Commun. **79**, 124 (1994).

[68] R. Stumpf and M. Scheffler, Computer Phys. Commun. **79**, 447 (1994).

[69] D. Fisher and R. D. Diehl, Phys. Rev. B **46**, 2512 (1992); S. Chandavarkar and R. D. Diehl, Phys. Rev. B **40**, 4651 (1989); R. D. Diehl, in *Phase Transitions in Surface Films 2*, ed. H. Taub (Plenum Press, New York, 1991).

[70] J. Neugebauer and M. Scheffler, to be published.

[71] Note that in an earlier work [21,31] the adsorption and binding energies (equs. 14, 15, 17) were defined with opposite sign. Throughout this paper we adopt the sign convention that for an exothermic process the adsorption energy is positive.

[72] J. Wang, Z. C. Ying, and E. W. Plummer, to be published.

[73] J. O. Porteus, Surf. Sci. **41**, 515 (1974).

[74] H. Brune, Ph.D. thesis, Freien Universität Berlin, 1992.

[75] H. Brune, J. Wintterlin, R. J. Behm, and G. Ertl, Phys. Rev. B, in press.

[76] A. Schmalz, S. Aminpirooz, and J. Haase, Surf. Sci. **301**, L211 (1994).

[77] R. Fasel, P. Aebi, J. Osterwalder, L. Schlapbach, R. G. Agostino, and G. Chiarello, to be published.

[78] In the XPD study the third interlayer spacing was assumed to be the same as the first interlayer spacing of the $(\sqrt{3} \times \sqrt{3})R30°$-Na/Al(111) structure.

[79] B. Hutchins, T. Rhodin, and J. Demuth, Surf. Sci. **54**, 419 (1976).

[80] M. Van Hove, S. Y. Tong, and N. Stoner, Surf. Sci. **54**, 258 (1976).

[81] J. N. Andersen, E. Lundgren, R. Nyholm and M. Qvarford, Phys. Rev. B **46**, 12784 (1992).

[82] S. Aminpirooz, A. Schmalz, N. Pangher, J. Haase, M. M. Nielsen, D. R. Batchelor, E. Bøgh, and D. L. Adams, Phys. Rev. B **46**, 15594 (1992).

[83] R. Stumpf and M. Scheffler, Phys. Rev. B, in press (1995).

[84] P. J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).

[85] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[86] D. M. Newns, Phys. Rev. **178**, 1123 (1969).

[87] B. Wenzien, J. Bormet, J. Neugebauer, and M. Scheffler, Surf. Sci. **287/288**, 559 (1993).

[88] H.M. Polatoglou, M. Methfessel, and M. Scheffler Phys. Rev. B **48**, 1877 (1993).

[89] K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins, and A. M. Bradshaw, Phys. Rev. Lett. **61**, 2488 (1988).

[90] J. Paul, J. Vac. Sci. Technol. **A5**, 664 (1987).

FIG. 1. Schematic representation of the emptying and broadening of the alkali metal atomic s level as it approaches a metal surface. Φ_s and $\Delta\Phi$ represent the substrate work function and the change in the substrate work function, respectively, and E_F and I_a denote the Fermi level of the substrate and the first ionization energy of the free adatom. The figure is drawn with values which resemble the adsorption of Na on Al(111) at low temperature and low coverage ($\Theta \approx 0.1$).

FIG. 2. Change in work function with increasing coverage obtained by Lang [2] using a jellium on jellium model for parameters corresponding to Na on Al(111).

FIG. 3. (a) Change in the density of states due to adsorption of sodium (dashed), silicon (dot-dashed), and chlorine (dotted) on Al (111) (from Ref. [61]). The density of states of the aluminum substrate is shown as a solid line. Energies are given with respect to the Fermi level which is indicated by a vertical full line. The vertical dashed line indicates the bottom of the valence band. (b) Analogous quantities to (a) for a jellium substrate with an electron density which is approximately equal to the average value of Al: $r_s = 2$ bohr. Li is considered instead of Na (after Fig. 2 of Ref. [6]).

FIG. 4. Total valence electron density in a plane perpendicular to the surface in the $[1\bar{2}1]$ direction for the chemisorption of sodium, silicon, and chlorine (from left to right) on Al (111). The contour spacing is $29 \times (1.5)^k \times 10^{-3}$ bohr^{-3} with $-5 \leq k \leq +5$. The green-yellow boarder line ($k = 0$, $n(\mathbf{r}) = 29 \times 10^{-3}$ bohr^{-3} is the average density of the aluminum, i.e., $r_s = 2.02$ bohr.

FIG. 5. Density difference, $n(\mathbf{r}) - n^0(\mathbf{r}) - n^{\mathrm{atom}}(\mathbf{r})$, for Na, Si, and Cl on Cu (111) (upper panel) and on Al (111) (lower panel) in a plane perpendicular to the surface in the $[1\bar{2}1]$ direction (from Ref. [62]). $n(\mathbf{r})$, $n^0(\mathbf{r})$, and $n^{\mathrm{atom}}(\mathbf{r})$ are the electron densities of the adsorbate system, the clean surface, and the free, neutral adatom. The hatched areas correspond to regions of charge increase and the unhatched areas correspond to charge depletion. The units are 10^{-3} bohr^{-3} and the contour lines correspond to the values -5.0, -2.5, -0.5, 0.0, 0.5, 2.5, and 5.0 .

FIG. 6. (a) Adsorption energy versus coverage for K in on-top and fcc-hollow sites on Al (111). The dashed line marks the phase transition from the homogeneous adlayer into adatom islands with a $(\sqrt{3} \times \sqrt{3})R30°$ periodicity (from Ref. [31]). (b) Adsorption, $E_{\mathrm{ad}}^{\mathrm{sub}}$, and binding energies, E_b^{sub}, for substitutional adsorption, and vacancy formation energy, E_f^{vac}, versus coverage (from Ref. [70]).

FIG. 7. Perspective view of the atomic structure of $(\sqrt{3} \times \sqrt{3})R30°$-K on Al (111). (a) K atoms (red) are in on-top sites and the substrate atoms under the potassium atoms (yellow) are displaced towards the bulk and the substrate atoms between the potassium atoms (blue) are displaced upwards with respect to the ideal positions. (b) Substitutional geometry where the Al atoms which were beneath the K atoms in (a) have been kicked out.

FIG. 8. Adsorption energy versus coverage for Na in on-top and fcc-hollow sites on Al (111). The dashed line marks the phase transition from the homogeneous adlayer into adatom islands with a condensed structure (from Ref. [31]). (b) Adsorption, $E_{\mathrm{ad}}^{\mathrm{sub}}$, and binding energies, E_b^{sub}, for substitutional adsorption, and vacancy formation energy, E_f^{vac}, versus coverage (from Ref. [70]).

FIG. 9. Perspective view of (a) the condensed hexagonal (4×4)-Na/Al (111) surface structure, (b) $(\sqrt{3} \times \sqrt{3})R30°$-Na/Al (111) with Na in the surface substitutional site, and (c) the (2×2)-Na/Al (111) surface alloy structure. The purple, blue, and green circles represent, respectively, Na atoms and Al atoms in the first and second layer. In (c) the Al atom in the hcp-hollow site of the surface alloy is shown in yellow and the inequivalent Na atoms are depicted by different shades of purple.

FIG. 10. (a) Adsorption energy versus coverage for Na on Al (001) in the on-surface hollow site and in the surface substitutional site. (b) Adsorption, $E_{\mathrm{ad}}^{\mathrm{sub}}$, and binding energies, E_b^{sub}, for substitutional adsorption, and the vacancy formation energy, E_f^{vac}, versus coverage (from Ref. [37]).

FIG. 11. Perspective view of the atomic structure of $c(2 \times 2)$-Na on Al (001). The purple, blue, and green circles represent, respectively, Na atoms and Al atoms in the first and second layer. (a) On-surface hollow site geometry and (b) substitutional geometry, where every second Al atom in the top unreconstructed Al layer has been kicked out.

FIG. 12. (a) Surface dipole moment for homogeneous adlayers of Na on Al (111) in the fcc-hollow site and in the surface substitutional site versus coverage. (b) The corresponding change in the work function where the same symbols as in (a) are used (after Ref. [70]).

FIG. 13. Calculated (dashed line) and measured (full line with open circles) work function change, $\Delta\Phi$, with coverage for K on Al (111). (a) For "low temperature" and (b) for "high temperature" (from Ref. [31]). The experimental results are from Ref. [89].

FIG. 14. Change of the electron density for $(\sqrt{3} \times \sqrt{3})R30°$-K on Al (111) for K in (a) the on-top site and (b) the substitutional site. For the on-top site the reference system is the clean surface and for the substitutional site it is the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure. The contours are in the plane normal to the surface and parallel to the $[1\bar{2}1]$ direction. The substrate atoms are represented by the small dots and the K atoms by the large dots. The units are 10^{-3} bohr^{-3} (from Ref. [21]).

FIG. 15. Calculated (dashed line) and measured (full line with open circles) work function change, $\Delta\Phi$, with coverage for Na on Al (111). (a) For "low temperature" and (b) for "high temperature" (from Ref. [31]). The experimental results are from Ref. [46].

FIG. 16.　　Change of the electron density for $(\sqrt{3} \times \sqrt{3})R30°$-Na on Al (111) for Na in the substitutional site. The reference system is the $(\sqrt{3} \times \sqrt{3})R30°$ surface vacancy structure. The contours are in the plane normal to the surface and parallel to the $[1\bar{2}1]$ direction. The substrate atoms are represented by the small dots and the Na atoms by the large dots. The units are 10^{-3} bohr^{-3} (from Ref. [21]).

FIG. 17.　Change of the electron density for the (2×2)-Na/Al (111) surface alloy structure The reference system is the Al (111) surface plus the reconstructed Al layer and the Al atom in the hcp-hollow site on the reconstructed layer. The contours are in the plane normal to the surface and parallel to the $[\bar{1}\bar{1}2]$ direction. The Al atoms are represented by the small dots and the Na atoms by the large dots. The units are 10^{-3} bohr^{-3} (from Refs. [51]).

FIG.　　　　　18.　　　　　　Change of the electron density for $c(2 \times 2)$-Na/Al (001) with the Na atoms in the substitutional site. The reference system is the $c(2 \times 2)$ surface vacancy structure. The contours are in the plane normal to the surface and parallel to the [110] direction. The Al atoms are represented by the small dots and the Na atoms by the large dots. The units are 10^{-3} bohr^{-3} (from [37]).